EFFECT OF POST TREATMENT PARAMETERS ON CORROSION RESISTANCE OF Ti-13Nb -13Zr COATED WITH HYDROXYAPATITE VIA ELECTROPHORETIC DEPOSITION

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*I would like to dedicate this project report to my **God** Almighty who has been eternal rock and source of refuge*

*Also this project report is dedicated to my beloved parents **Amal** and **Najm** as well as my sisters and brothers who have supported me during my study period*

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ABSTRACT

Recently, applications of Ti-13Nb-13Zr alloy have been widely increased in biomedical fields due to its excellent biocompatibility and mechanical properties. However, its corrosion resistance is still a matter of concern when it is implanted inside human body. Many attempts have been done to enhance its corrosion resistance by using hydroxyapatite coating. This study includes two major directions; firstly calcium phosphate was electrophoretically coated on Ti-13Nb-13Zr surface in order to improve its corrosion resistance. Sintering post treatment was then conducted to the coated samples in order to transform the deposited layer from dicalcium phosphate dehydrated (DCPD) phase to the hydroxyapatite crystalline (HA) phase. The effect of two different sintering post-treatment parameters including time and temperature have been experienced on the corrosion potential of calcium phosphate coated substrate. Full factorial experimental designs followed by Response Surface Methodology (RSM) were employed for planning and analyzing the experimental results. Time and temperature of sintering post-treatment were considered as independent variables while corrosion potential is accounted as a response variable. Empirical models were successfully developed to predict amount of corrosion potential by using design of experiment (DOE) software. Experimental results show that the effect of sintering temperature is more significant than the sintering time. Moreover the results indicate that high corrosion potential is obtained under sintering conditions at (Time = 90 minutes, Temperature = 700° C). Finally, the electrophoretic deposition method exhibits a relatively uniform HA coating layer and free of crack.

ABSTRAK

Kebelakangan ini, aplikasi aloi Ti-13Nb-13Zr telah meningkat secara meluas dalam bidang bioperubatan kerana keserasian-bio dan sifat-sifat mekaniknya yang sangat baik. Walau bagaimanapun, ketahanan kakisannya masih menjadi perhatian apabila ia diimplankan ke dalam badan manusia. Banyak usaha telah dilakukan untuk meningkatkan rintangan kakisan dengan menggunakan salutan hydroksiapatit. Kajian ini merangkumi dua halatuju utama; pertama kalsium fosfat di salutkan ke atas permukaan Ti-13Nb-13Zr secara elektroforesis bagi meningkatkan ketahanan kakisannya. Pasca rawatan pensinteran telah dijalankan kepada sampel bersalut untuk mengubah lapisan daripada fasa dikalsium fosfat dehidrasi (DCPD) kepada fasa kristal hydroksiapatit (HA). Kesan dua parameter selepas rawatan pensinteran yang berbeza termasuk masa dan suhu telah di kaji berdasarkan kepada keupayaan kakisan ke atas substrat kalsium fosfat bersalut. Rekabentuk ujikaji faktoran penuh diikuti oleh Kaedah Respon Permukaan (RSM) telah digunakan untuk merancang dan menganalisis keputusan ujikaji. Masa dan suhu pensinteran selepas rawatan dianggap sebagai pembolehubah bebas manakala potensi hakisan diambil kira sebagai pembolehubah respon. Model empirikal telah berjaya dibangunkan untuk meramalkan jumlah potensi kakisan dengan menggunakan perisian reka bentuk ujikaji (DOE). Keputusan ujikaji menunjukkan kesan suhu pensinteran adalah faktor yang lebih signifikan berbanding masa pensinteran. Selain itu, keputusan menunjukkan bahawa potensi kakisan yang tinggi diperolehi dalam keadaan pensinteran pada (Masa = 90 minit, Suhu = 700 °C). Akhir sekali, kaedah pemendapan elektroforetik menunjukkan bahawa lapisan salutan HA yang disebabkan oleh pensinteran selepas rawatan adalah agak seragam dan bebas daripada retakan.

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LIST OF ABBREVIATIONS

ANOVA		Analysis of variance
DCPD	-	Dicalcium phosphate dihydrated
DF	-	Degree of freedom
DOE	-	Design of Experiment
E_{corr}	-	Corrosion potential
EDS	-	Energy dispersive spectrometer
EPD	-	Electrophoretic deposition
HA	-	Hydroxyapatite
MS	-	Mean square
RSM	-	Response surface methodology
SBF	-	Simulated body fluid
SEM	-	Scanning electron microscope
SS	-	Sum of square
XRD	-	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Biomaterials have a long history as orthopaedic implants and bone graft substitutes due to their well-known strength (elastic modulus larger than 100 GPa), particularly in load-bearing areas. The advantages of biomaterials include excellent mechanical properties such as fatigue, reasonable corrosion resistance, biocompatibility, suitable density, high strength and biocompatibility. The heat treatment and manufacturing method also affect these properties. Their use is however associated with several limitations, which comprise permanence, cracking, low volumetric porosity, relatively high modulus of elasticity, low osseointegration with bone tissues and the potential of releasing metallic ions which in turn resulting in a corrosion within the body. Most metals have ability to produce a complete tissue replacement for bone defects due to their biodegradable properties.

Corrosion is a great concern for use of metallic implant when it exposed in hostile electrolytic environments because the corrosion products have been implicated in causing infections, local pain, swelling, and loosening. It can, therefore, severely limit the fatigue life and ultimate strength of the material, leading to the in vivo failure of implants [42]. The human body shows natural reaction against prosthetic devices causing the osteolysis and has the tendency to isolate from the surrounding live tissues.

In order to improve corrosion resistance, biodegradation and bioactive properties, bio-ceramic coatings on metallic substrates have been widely used in bone substitutes because of their biocompatibility, bioactivity, and osteoconductivity. Surface engineering processes can be used increasingly either to modify existing surfaces or to apply coatings. Coating can be applied for a diversity of reasons. As the corrosion of metal surface is an electrochemical reaction between the metal and external agents (for example, oxygen and/or water). Coating can act as a barrier and preventing this reaction.

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is composed primarily of calcium and phosphorous with hydroxide ions that are eliminated at elevated temperatures. HA and other related calcium phosphate minerals have been utilised extensively as implant materials for many years due to its excellent biocompatibility and bone bonding ability and also due to its structural and compositional similarity to that of the mineral phase of hard tissue in human bones [43]. HA coatings have good potential as they can exploit the biocompatible and bone bonding properties of the ceramic, while utilising the mechanical properties of substrates such as Co-Cr alloys, Ti based alloy and other biocompatible alloys. While the metallic materials have the required mechanical properties, they benefit from the HA which provides an osteoconductive surface for new bone growth, anchoring the implant and transferring load to the skeleton, helping to combat bone atrophy have been extensively used for the purpose of bone graft substitute and bone tissue engineering. Because of their similarity to bone mineral, calcium phosphorous (Ca/P) based materials are biocompatible, osteoconductive and bone-bonding.

In orthopaedic field, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) coated metal implants have been studied extensively due to their outstanding biological responses in the physiological environment and surface protection against body fluid [44]. Several coating methods have been introduced for coating of HAp on the metallic substrates: plasma spraying, sol–gel, RF magnetron sputter, ion beam dynamic mixing, pulse laser deposition, biomimetic coating, electrophoretic deposition, and electrolytic deposition. Among the various fabrication methods, electrophoretic deposition (EPD) is a promising technique, with advantages including short formation time, simplicity in instrumentation, and capability of coating complex-shaped implants. Electrophoretic deposition is a colloidal processing technique that allows not only shaping free standing objects but also allows depositing thin films and coatings on substrates. EPD is known to be one of the most effective and efficient techniques to assemble fine particles. This technique has received significant attention due to its simplicity in setup, low equipment cost, and capability to form complex shapes and patterns. EPD is also a potentially attractive process for obtaining bioceramic. The application of EPD in the biomaterials area, in particular for obtaining HAp and bioactive glass coatings on metallic implants, has been demonstrated [45].

Electrophoretic deposition (EPD) was used in the current work as the coating technique due to its efficiency, flexibility, and economy. In general, a short deposition time is required for electrophoretic forming or coating (a few seconds to a few minutes). The deposition rate of electrophoresis can be as high as 1 mm/min. Uniform coatings of complex shapes can be easily formed by using appropriately shaped electrodes, such as wire, coil or plate. A high degree of control of coating deposit morphology can be obtained by adjusting the deposition conditions, the ceramic powder size and shape. However with increasing deposition time and voltage, the thickness of the coating increases.

Evaluation the electrochemical corrosion behaviour of HA coating layer on the Ti-13Nb-13Zr substrate is one of the goals of this project. It is expected the coating of HA layer to improve the corrosion resistance by this project's method.

1.2 Problem Statement

Nowadays corrosion of the biomaterials becomes a significant issues the corrosion behaviour of various implants and the role of the surface oxide film and the corrosion products on the failure of implants are discussed. Nonetheless, these problems would be solved by coating implants with biocompatible and corrosion resistant material like Hydroxyapatite (HA). Electrochemical deposition of HA following by sintering post-treatment on metallic implant has unique advantages due to its capability of forming uniform coating and simple setup. But there is still lack of research and study on controlling of post-treatment parameters including time and temperature after EPD coating on Ti-13Nb-13Zr substrate.

1.3 Objectives of the Study

Based on the problem statement of the project, the objectives of this research were:

i. To evaluate the effect of post-treatment parameters (sintering time and temperature) on corrosion resistance of HA coated Ti-13Nb-13Zr alloy.
ii. To determine the optimal setting of post treatment parameters for better corrosion resistance of (Ti-13Nb-13Zr) substrate.

1.4 Scopes of the Study

The scopes of this project were:

i. The implant material used in this study was limited to one of the metallic implant material which is Ti-13Nb-13Zr alloy.
ii. Coating performances were evaluated in terms of corrosion resistance and micro-crack formed after sintering post-treatment.
iii. Electrophoretic deposition technique (EPD) was employed for coating of HA on Ti-13Nb-13Zr alloy.
iv. Design Expert 7 software (DOE) was used to analyse the experimental results.
v. Two different sintering parameters including time and temperature were used to evaluate their effects on the corrosion resistance of HA coated layer.

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